Neutral Composition of the Upper Atmosphere of Mars as Determined from the Mariner UV Spectrometer Experiments

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ABSTRACT

Atomic oxygen (O) and hydrogen (H) have been identified in the spectra of the upper atmosphere of Mars by the Mariner 6 and 7 Ultraviolet (UV) Spectrometer Experiment. In addition, the presence of carbon monoxide (CO) is inferred by self-absorption in the fourth positive emission of CO. We review the current status of our quantitative knowledge of the O densities derived from an analysis of the OI 1356 and 1304 Å emissions. Emphasizing the uncertainties in the quantitative description of the excitation sources of these lines, we present the preliminary results from a study now in progress of an atomic oxygen density profile which best fits the Mariner 1304 Å data. This model predicts the correct 1356 Å emission within a factor of 2. Upper and lower limits are placed on the CO density from an analysis of the (1,0) band of the (A–X) system of CO. We describe the results in terms of a percentage composition of O and CO at the ionospheric peak at 135 km. The O concentration is ~3% and the CO concentration ~0.3% of the CO2 density at this level. Below the level where the O:CO ratio is unity, the atmosphere is expected to be nearly uniformly mixed, with a decreasing mixing ratio of CO with decreasing height. This level in the atmosphere, identified as the turbopause, is near the 100-km level, but may be as high as 120 km.

1. Introduction

During the near-encounter phases of the 1969 Mariner 6 and 7 missions to Mars, the UV spectrometer experiment measured emission spectra issuing from the sunlit upper atmosphere. A preliminary analysis of the Mariner 6 dayglow spectrum (Barth et al., 1969) described the identification of molecular bands of ionized carbon dioxide (CO2+) and carbon monoxide (CO), and lines of atomic oxygen (O), carbon (C), hydrogen (H), and possible sources of these emissions. The origin of the CO2+ bands were further discussed by Dalgarno et al. (1970). A recent report (Barth et al., 1971) describes a comprehensive spectroscopic analysis of all the Mariner bright limb spectra. In addition, this report contains the results of integrations over individual spectral features, with the removal of scattered light effects. This latter type of information has been recently analyzed by Stewart (1971), with the aid of a model thermosphere based on thermal balance calculations. His model requires a low efficiency of solar UV heating, and an exospheric temperature (~350K) that is lower than pre-Mariner predictions of Stewart and Hogan (1969). It is also lower than expected on the basis of McElroy's thermal model (1969).

We will review the current status of the analysis of information contained in the Mariner spectra on the minor constituents in the Martian atmosphere. So far, only O and H have been positively identified. The consequences of an upper limit to N2 and N2+ emissions on the lower atmospheric nitrogen content have been considered by Dalgarno and McElroy (1970). The absence of an atomic carbon scale height in the altitude variations of the CI 1561 and 1657 Å lines has been used to derive upper limits to carbon atom concentrations (McElroy and McConnell, 1971). An analysis of the hydrogen Lyman-alpha measurements has been recently reported by Anderson and Hord (1971) who derive an atomic hydrogen density of 3±1×10^4 cm^-3 at 250 km. Their results substantiate the low exospheric temperature of ~350K needed in Stewart's model to reproduce the scale heights of the various band systems at the lower altitudes. The presence of H is almost certainly a result of water vapor dissociation in the lower atmosphere (Barth, 1969; Hunten and McElroy, 1970).

We now focus our attention on the information bearing on the two remaining constituents of interest, O and CO2, and, in particular, on the concentrations of the two principal dissociation products of CO2. We will review the most recent results of a study of the OI 1304 Å radiative transfer problem that is being carried out at our Laboratory. Some preliminary results for the atomic oxygen concentration (one part in a thousand at the F1 peak) were reported by Thomas (1969). These early estimates have since been replaced by more reliable values of 1–10% (Thomas, 1970). (Unfortunately, it was the earlier estimate that received the most attention and which was most widely quoted.) These analyses were hampered by an absence of laboratory data on
excitation cross sections of 1304 and 1356 Å, and by the use of an approximate solution to the 1304 Å radiative transfer equation whose accuracy could not be readily checked. The problem of the source strength has recently been eased with availability of the recent laboratory measurements of Stone and Zipf (private communication). We now have accurate solutions to the appropriate radiative transfer problem through the application of a technique of solution first developed by Strickland and Donahue (1970). We will describe some preliminary results from a study of the oxygen problem now being carried out by Strickland in collaboration with the author. In addition, some new results are reported for the carbon monoxide composition deduced from an analysis of the A-X fourth positive bands. We will then present a model atmosphere for CO₂, CO, and O using Stewart's (1971) model of the thermal structure.

2. The OI 1304 and 1356 Å lines and the CO fourth positive bands

The intensities of the 1302, 5, 6 Å resonance triplet of O(\(\text{^3}P_{0,1,2} \rightarrow \text{^3}S_{1}\)), the 1356, 8 Å doublet of O(\(\text{^3}P_{1,2} \rightarrow \text{^3}S_{2}\)), and the A-X fourth positive band system of CO(A'\(\Pi_{a} \rightarrow X'\Sigma^{+}\)) are shown as a function of minimum ray height in Fig. 1. The geometry of the near-encounter viewing angles of the UV spectrometer experiments is described by Barth et al. (1971). All intensities have been averaged over four limb crossings. The 1304 Å measurements have been averaged within successive 20-km intervals. The error bars represent the standard deviations of the average. There is some question as to the significance of this particular average, since there appear to be some systematic differences between the measurements taken during different limb crossings. The observed systematic differences, if they are real, cannot be explained unless real changes occurred in the atmosphere or in the excitation sources. However, we are concerned only with the general magnitude of the intensity and the general shape of the altitude variation.

Note the dramatic difference between the two atomic oxygen emissions, even though both are largely due to excitation by photoelectron impact on ambient atomic oxygen. Whereas O is optically thin in the 1356 Å lines, it is optically thick in the 1304 Å lines; the latter radiation "diffuses" to great heights before it escapes the medium.

The fourth positive bands exhibit the scale height of CO₂ in Stewart's model. It is reasonably certain that they arise mainly from photoelectron impact dissociation of solar photodissociation of CO₂, ending in an excited \(^1\Pi\) CO fragment (Barth et al., 1971). The ab-
Table 1. Excitation mechanisms in atmosphere of Mars.

<table>
<thead>
<tr>
<th>Excitation process</th>
<th>( \text{OI} , (\text{P}^\text{+} \rightarrow \text{S}) )</th>
<th>( \text{OI} , (\text{P}^\text{+} \rightarrow \text{S}) )</th>
<th>( \text{CO} , (\text{A} \rightarrow \text{X}) \</th>
</tr>
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<tbody>
<tr>
<td>1304 Å</td>
<td>1356 Å</td>
<td>1400–1800 Å</td>
<td></td>
</tr>
<tr>
<td>Resonance scattering</td>
<td>( g_{ps} = 6.7 \times 10^{-7} )</td>
<td>Transition optically forbidden</td>
<td>( g_{ps} = 1.66 \times 10^{-7} ) [using ( f ) value of Lassette and Skerbele (1971)]</td>
</tr>
<tr>
<td>(Barth, 1969)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photoelectron excitation</td>
<td>( \sigma_{\text{max}}(16 \text{ eV}) = 1.3 \times 10^{-10} \text{ cm}^2 )</td>
<td>( \sigma_{\text{max}}(0.5 \text{ eV}) = 1.9 \times 10^{-17} \text{ cm}^2 )</td>
<td>( \sigma_{\text{max}} = 4.35 \times 10^{-15} \text{ cm}^2 ) at ( E = 20 \text{ eV} )</td>
</tr>
<tr>
<td>(Stone and Zipf)**</td>
<td>(Stewart, 1965)</td>
<td></td>
<td>(Ajello, 1971)</td>
</tr>
<tr>
<td>Photodissociative excitation from ( \text{CO}_2 )</td>
<td>( \lambda &lt; 829 , \text{Å} ) Theoretical threshold</td>
<td>( \lambda &lt; 830 , \text{Å} ) Theoretical threshold</td>
<td>( \lambda &lt; 908 , \text{Å} ) Theoretical threshold for 1510 Å (1.0 emission)</td>
</tr>
<tr>
<td></td>
<td>( \sigma_{\text{max}}(100 \text{ eV}) = 7.6 \times 10^{-29} \text{ cm}^2 )</td>
<td>( \sigma_{\text{max}}(100 \text{ eV}) = 7.6 \times 10^{-38} \text{ cm}^2 )</td>
<td>( \sigma_{\text{max}} = 1.36 \times 10^{-48} \text{ cm}^2 ) at ( E = 21 \text{ eV} )</td>
</tr>
<tr>
<td></td>
<td>(Ajello, 1971)</td>
<td></td>
<td>(Ajello, 1971)</td>
</tr>
</tbody>
</table>

* Dominant mechanism.
** Personal communication.

ence of a CO scale height gives an upper limit to the solar resonance scattering of ambient CO molecules.

a. Sources of excitation of 1304 Å

The dominant excitation mechanisms are probably photoelectron excitation of O and resonance scattering of the 1304 Å solar lines. The photoelectron dissociative excitation from \( \text{CO}_2 \) is a negligible source of 1304 Å because of the small cross section for this process in the low-energy region of the photoelectron energy spectrum. The rate for the same process induced by solar photons has not yet been measured. Since there is an ample supply of solar energy below 829 Å, this process may be an important source of 1304 Å. However, we will later argue that it cannot be the major source.

To calculate the primary excitation rate \( S_0(\lambda) \) (photons cm\(^{-2}\) sec\(^{-1}\)) from photoelectron impact on O, we must know the photoelectron energy distribution. This involves a detailed study of the production and loss processes as a function of energy and altitude. Stewart (1970, 1971) has shown that the results of such a calculation for the earth's atmosphere are largely a function of only one variable, the slant column density \( N \) of the major constituents. This has also been shown to be true for a predominantly \( \text{CO}_2 \) atmosphere. The excitation rate may be expressed as

\[
S_0(\lambda) \approx g_{pe}(N) n(O, \lambda),
\]

where \( g_{pe} \) is a constant for small \( N \) and varies roughly as \( N^{-2} \) for large \( N \). We have used values for \( g_{pe} \) calculated for a pure \( \text{CO}_2 \) atmosphere by A. I. Stewart (private communication) which have been scaled to take into account recent laboratory cross section measurements of Stone and Zipf (see Table 1). The value of \( g_{pe}(N = 0) \), taken to be \( 1 \times 10^{-4} \) photons atom\(^{-1}\) sec\(^{-1}\) must be regarded as a preliminary value to be revised when more accurate calculations become available. Recent measurements of terrestrial 1304 Å airglow by a UV photometer on the satellite OGO-6 (Strickland and Thomas, 1971) indicate that the value for \( g_{pe} \) adopted for Mars may be too large. (This is probably compensated for to some extent by our use of values for the line-center solar fluxes for 1304 Å which the OGO-6 analysis indicates are probably too small.) Although the situation is improved over that of a few years ago, there is still an uncomfortable degree of uncertainty in the photoelectron excitation rates. We regard the results presented here as indicative of the 1304 Å sources to be expected in the Martian upper atmosphere, but far from definitive.

Our knowledge of the solar 1304 Å fluxes should be much more satisfactory. Unfortunately, rather different fluxes in the three lines have been reported in the literature varying by nearly a factor of 3. The flux values in the present calculation were taken from a recent review by Hinteregger (1970). The important quantity for the resonance scattering calculation is not the total flux in the lines, but the values of the fluxes within \( \sim 0.1 \) Å of the line centers. The 1302, 1305 and 1306 Å line widths have been measured to high resolution in a rocket flight by Brunner and Rense (1969) to be 0.26, 0.22 and 0.16 Å, respectively. The removal of the influence of the deep absorption core due to terrestrial oxygen above the rocket is highly uncertain (Brunner et al., 1970). Using the flux values of Hinteregger (1970), the line center fluxes for the solar 1302, 1305 and 1306 Å lines are 2.1, 2.3 and 3.1 (all in units of \( 10^9 \) photons cm\(^{-2}\) sec\(^{-1}\) Å\(^{-1}\)).

b. Sources of excitation of 1356 Å

Here the situation is somewhat improved over the 1304 Å lines since there are fewer possible ways of exciting 1356 Å emission. Impact of photoelectrons on oxygen is probably the most efficient source. The \( g_{pe} \) factor for this process is \( \sim 2.2 \times 10^{-8} \) for \( N = O \), using the theoretical cross sections given by Stewart (1965). Resonance
scattering is forbidden. Possible contributions from CO$_2$ dissociation products may be important. The values for the photoelectron excitation cross section by Ajello (1971) are probably too low (Stone and Zipf, private communication) since no account was taken of the high velocities of the O(1S) atoms formed in the dissociation process. Most of the long-lived excited atoms would have left the field of view of Ajello's apparatus before radiating. There are no measurements available for the corresponding photodissociation process.

c. Sources of excitation of CO(A–X) emission

The fourth positive bands may arise from solar resonance scattering from ambient CO, or from photodissociation or electron impact dissociation of CO$_2$ with the formation of an excited $^2$II state of CO (Barth et al., 1971). The vibrational distribution of laboratory spectra of CO emission induced by 20-eV electrons on CO$_2$ matches closely that of the Mariner spectra, except that in the latter the (v',0) bands are largely missing (Fig. 2). Neither the laboratory spectrum for electrons on CO nor the expected vibrational distribution of bands produced by resonance scattering matches the observed spectrum (Barth, private communication). Furthermore the scale height of the A–X system follows that of CO$_3$, not CO$_2$.

The possible sources for the three different emissions are summarized in Table 1. The $g$ factor for resonance scattering is defined as the number of solar photons scattered per atom (or molecule) per second for an unattenuated solar flux. The $g$ factor for 1304 Å given by Barth (1969) agrees closely with our calculations at altitudes $>650$ km. The $g$ factor for the (1,0) band of the CO (A–X) is also taken from Barth (1969), except that the value is multiplied by 1.8 to account for an improved value of the oscillator strength measured by Lassette and Skerbele (1971).

d. Radiative transfer in the 1304 Å lines

We define the oxygen model as the percentage of atomic oxygen present at the F1 peak (135 km). Even for small amounts of O relative to CO$_2$, the atmosphere is optically thick at 1304 Å. For a 1% model, the vertical optical depths above 135 km in the three lines $\tau_j$ ($j=0$, 1306 Å; $j=1$, 1305 Å; $j=2$, 1302 Å) are $\tau_2=207$, $\tau_1=66$, and $\tau_0=17$. The ratios of $\tau_j$ vary as the relative populations $P_j$ of the ground states, determined by the Boltzmann distribution to very high altitudes. The trapping, or radiative imprisonment, of the photons is governed mainly by the optical thickness in the 1306 Å line, since these photons most readily escape from the atmosphere.

For a given distribution of primary excitation $S_0(\tau_j)$, the source function for the true emission rate $S(\tau_j)$ is given by

$$S(\tau_j) = S_0(\tau_j) + \sum_{k=1}^3 \int d\tau_{k'} g_k(P_k/P_j)$$

$$\times H(|\tau_k - \tau_{k'}|, |t-t'|) S(\tau_{k'}) ,$$

where $g_k$ is the statistical weight of the $j$th ground level, $H$ the transport kernel, and $t$ and $t'$ the vertical optical depths for pure absorption by CO$_2$ at the heights $z$ and $z'$. The optical depth $\tau_j$ is given by

$$\tau_j(z) = \int_z^\infty k_0 P_j n(O,z') dz',$n_0$$

being the cross section at line center, independent of the particular line. Strickland and Donahue (1970) have
solved Eq. (2) for the earth’s 1304 Å dayglow emission, under the assumption of a plane-parallel atmosphere. We have applied similar techniques to the solution of the present problem. Our results for the source function $S(z)$ for both photoelectron excitation and solar resonance scattering are shown in Fig. 3. We have used a 3% model and the temperature profile shown in Fig. 7, taken from Stewart’s (1971) paper. The radiative transfer amplification of the excitation rates is over 100 for this model.

The calculation of the 1304 Å intensity for the geometry of the Mariner fly-by is accomplished by including the sphericity of the atmosphere in the expression

$$4\pi I = \sum_j \int d\tau_j S(\tau_j) T(\tau_j,\tau'),$$

where $T$ is the transmission function for resonance scattering. As the resolution of the instrument is 10 Å, only the sum of the three lines is measured. Since the Mariner spectrometer viewed the atmosphere tangentially, the integration over $d\tau_j$ is weighted heavily by the sources near the point of closest approach of the ray to the planet. Note that we have assumed a plane geometry in calculating $S(\tau_j)$, but have included the spherical geometry in the calculation of the intensity. This is a valid assumption for the Martian atmosphere whose effective thickness is much smaller than the radius of curvature. It results from the fact that the source function over most of the medium is dominated by photon escape in directions not far from the vertical, for which the plane-parallel description is nearly correct.

e. Comparison with Mariner data

We have calculated the 1304 Å intensity from the above equations, including both photoelectron excitation and solar resonance scattering. The prediction for the 3% model, which best fits the data, is shown in Fig. 4. The satisfactory agreement of the predicted and observed 1304 Å altitude profiles demonstrates the basic soundness of the radiative transfer model. The assumption of a Doppler line profile for the lines gives a better fit to the altitude profile than that of a Voigt line profile. The important difference arises in the optically thick region (below 200 km) where the radiation more easily escapes the atmosphere in the line wings of the Voigt emission profile than in the Doppler profile. The escape of photons from the “side” of an optically thick plane-

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**Fig. 3.** Initial excitation rates, $S_0$, and true excitation rates, $S$, for the two primary sources of 1304 Å. The curves labeled “ph.el.” are the excitations from photoelectron impact on ambient atomic oxygen. These calculations apply to a 3% atomic oxygen model.

**Fig. 4.** Comparison of the calculations for the 1304 and 1356 Å limb intensities for the 3% model with the Mariner data. The Voigt and Doppler cases refer to the assumptions regarding the line profiles of the emitted and absorbed radiation within the 1304 Å lines.
tary atmosphere is sensitive to the assumed emission profile. Therefore, such calculations must be performed with care, insuring that deviations from the usual simple frequency redistribution are accounted for, and that proper attention is given to the altitude variation of the line profile due to a variation in temperature. As shown by Hummer (1969), use of a Doppler emission profile gives better results for the source function. It also more accurately describes the escape of photons from the cooler region (below 200 km) where the actual emission profile is narrower than for regions of higher temperature. If dissociative excitation of CO₂ were an important source of 1304 Å, we would expect the excited atoms to have initial speeds greatly in excess of the mean thermal speed. Consequently, the frequency of the prompt 1304 Å radiation would be Doppler-shifted well outside the resonance absorption line profile of the ambient oxygen. These photons would escape from the atmosphere directly and would be distributed in altitude like the CO (A-X) bands, that is, the measurements would follow the scale height of CO₂. No evidence of a sharp peaking in 1304 Å is present, thus excluding this mechanism as an important source.

The sensitivity of the radiative transfer calculations to changes in the oxygen model may be judged from the following: When the oxygen density is increased from a 1% to a 3% model, the photoelectron-produced intensity at the maximum increases by a factor of 3.7, while the solar-scattering intensity increases by only 25%. The sensitivity of the photoelectron-induced intensity is due to the fact that as density increases, both the initial excitation [given by Eq. (1)] and the radiative trapping increase. Since the latter is nearly balanced by the decrease in the transmission function [in Eq. (4)], the variation is mostly due to the variation in S(2). On the other hand, the primary excitation from solar scattering is not a linear function of density; it depends upon the product of the transmission function of solar radiation and the local number density. This product is a slowly varying function of density. The solutions show that for very small oxygen densities, the solar scattering produces most of the measured intensity. For increasing density, the photoelectron contribution increases rapidly. The cross-over point for the sources assumed here is at densities less than those in the Mars 3% model. It should be emphasized that the relative contribution of the two sources is a function of viewing geometry. At high minimum-ray altitudes, we would predict nearly equal amounts from the two sources, whereas at the maximum, the photoelectron contribution is 3.5 times as important as the solar source.

The calculated 1356 Å emission, assumed to be produced only by photoelectron impact on O, reaches a maximum intensity of 690 Rayleighs (R) at a height of 155 km, only 40% larger than observed (the theoretical curve is scaled downward in Fig. 4 to facilitate comparison of the shapes of the curves). This result is significant, since the oxygen model was chosen solely on the basis of the 1304 Å comparison. However, the agreement of the top-side slopes is unsatisfactory. The measurement of the 100 R intensity at 200 km could be used as evidence that a source arising from CO₂ is, in fact, dominant. However, the significance of a single point, particularly one of such low intensity, should not be overemphasized (it should be noted that the nominal sensitivity of the instrument is 70 R). The data are being re-examined, since there is an indication in the spectra taken at a minimum ray height of 220 km that the 1356 Å intensity will fall closer to the theoretical curve than that at 200 km. At any rate, if additional sources of 1356 Å are shown to be present, the atomic oxygen densities will be correspondingly lowered. This will produce difficulties in the 1304 Å comparison, as more efficient excitations for this emission must also be found.


Even though the major source of these bands is probably CO₂ dissociation-excitation, they are important in determining limits on the CO abundance. By assuming that the observed emission is entirely due to resonance scattering of the bands, we obtain a conservative upper limit to the CO abundance. By the weakness of the (v',0) bands in the observed distribution, we can infer a lower limit to the CO abundance by postulating that their low intensity is due to "self-absorption" from the v''=0 ground vibrational level.

The upper limit is derived from a knowledge of the resonance g factor (Barth, 1969) for a given band. For the (1,0) band, the g factor is given in Table 1. The upper limit to the CO density is related to the observed (1,0) intensity 4πI through the equation

$$n(\text{CO}) < \frac{4\pi I}{\ell (2\pi R_0 H)^4},$$

(5)

where R₀ is the distance to the center of the planet and H the scale height of CO. We have used the approximation that the Chapman function for a viewing angle of 90° is (πR₀/2H)¹. The observed intensities for this band at the viewing heights of 150 and 170 km are 927 and 312 R, respectively. For our thermal model the scale height at these altitudes is 21 km. Thus, the upper limits are n(1304 Å, 150 km)<8.4×10⁷ cm⁻³ and n(1304 Å, 170 km)<2.8×10⁷ cm⁻³.

To calculate the self-absorption of the (v',0) emission we must examine the detailed rotational distribution of the vibrational v' levels in emission and the v''=0 levels in absorption. The latter distribution is easily computed from the Boltzmann distribution (Herzberg, 1950), i.e.,

$$n_n = (2J+1)\left(\frac{hc}{kT}\right)^{-1} e^{-hcJ(J+1)/kT},$$

(6)

where n_n is the number of molecules in the Jth rotational
level, $J$ the angular momentum quantum number, $B_r$, the rotational constant for the $^3\Sigma$ state, and $\hbar$, $\epsilon$, $k$ and $T$ have their usual meaning; $n$ is the total number of CO molecules.

The distribution over the rotational levels in emission is complicated by the fact that the bands are believed to originate as an excited dissociation product; thus, we have

$$h\nu + (\epsilon) + \text{CO}_2(^3\Sigma, \nu, J) \rightarrow \text{CO}(^3\Pi, \nu', J') + \text{O} + (\epsilon) + \text{kinetic energy.}$$

Either a solar UV photon ($h\nu$) or a photoelectron ($\epsilon$) may induce the process. To satisfy the spin-conservation rule, the oxygen atom should be in the $^3\Pi$ or $^1\Sigma$ state. [However, this rule is apparently violated in laboratory excitation by UV photons, according to J. Mentall (private communication).] The initial rotational distribution of each of the $^3\Pi$ vibrational levels will be different from that of the original $\text{CO}_2(^3\Sigma)$ levels.

No experimental information exists for the rotational temperature of the bands originating from $\text{CO}_2$ dissociation. Theoretical studies by Krauss et al. (1971) indicate that up to 2 eV of rotational kinetic energy can be transferred to the excited CO molecule during the break-up of an intermediate (bent) mode of the $\text{CO}_2$ molecule. In the absence of experimental information, we have chosen two extreme cases for the rotational distribution of the emitted bands. In the first case, we suppose that they are the same as those of the $\text{CO}_2$ molecules in the atmosphere of Mars in the 150-km region. Since the moment of inertia of $\text{CO}_2$ is about five times larger than that of CO, the rotational levels are more closely spaced, and the distribution in the angular momentum quantum number $J$ extends out to $J \approx 50$ for $T = 350$K. When this distribution is transferred to an excited $^3\Pi$ level of CO, the emission of the A-X bands is rotationally “hot.” This distribution is shown as the dashed curve in Fig. 5. In the other extreme case, we suppose that the emission is “cold,” that is, the rotational distribution is the same as if the $^3\Pi$ levels were brought into collisional equilibrium before radiating. This is not a realistic assumption since the lifetimes of these levels are $\sim 1 \times 10^{-8}$ sec and collisions should play no role. The actual distribution is probably “hot” (and may well be even hotter than described in our extreme case).

We now return to the calculation of the self-absorption of the $(\nu', 0)$ levels by ambient CO in the atmosphere of Mars. For a column density $N(\text{CO})$ along the line of sight, the transmission of the atmosphere to radiation in the $(\nu', 0)$ band is given by

$$T(\nu', 0) = \sum J \left( \frac{n_J}{n} \right) T(J),$$

where $T(J)$ is the transmission function for the $J$th line whose line-center optical depth in the line of sight is given by

$$\tau_J = k_0(n_J''/n)N(\text{CO}),$$

$k_0$ being the cross section at line center, $2.3 \times 10^{-13}$ cm$^2$, for the $(1, 0)$ band. Note the important distinction between $n_J'$ and $n_J''$, the rotational distributions in emission and absorption, respectively. The transmission has been calculated for these two cases as a function of column density. The detailed absorptions within a band (actually in rotational space) are shown in Fig. 5 for the case of hot emission. Note that as the number of CO molecules increases, it becomes more and more difficult to absorb the emission at high $J$ numbers.

The energy that is re-absorbed by CO will largely be emitted in bands for which $\nu'' \neq 0$. However, a certain fraction will be re-emitted in the same bands. These may suffer additional re-absorption, and will again most likely be emitted in bands not ending on the ground state. We have ignored the small contributions that would occur because of an incomplete channeling into the $\nu'' = 0$ bands.

In Fig. 6 the transmission for the $(1, 0)$ band for the two cases is plotted as a function of the density of CO at the reference level, that is, at the point of closest approach of the ray to the planet. We now define the “observed transmission” as the ratio of the measured $(1, 0)$ band intensity to that which would have been present in the absence of self-absorption. This latter quantity is determined by obtaining a best fit of the laboratory spectrum (Fig. 8 of Barth et al., 1971) to the Mariner spectrum of the fourth positive system. The best fit is
made for those bands not ending on the ground state. For a minimum ray height of 150 km the average intensity of the (1,0) band was measured to be 378 R, compared with 927 R expected in the absence of self-absorption. The corresponding values for the 170 km height are 95 and 312 R. The observed transmission values are

Fig. 6. Variation of the transmission in the (1,0) band [(defined by Eq. (7)] with the density of CO at the reference level. The observed values for the transmission, defined in the text, are shown at two altitudes, 150 and 170 km. The "ε+CO2" curve applies to the "hot" model of the emission, where the J distribution is given in Fig. 5. The "ε+CO" curve applies to the "cold" model of emission, and assumes that the distribution over the angular momentum states is the same as that of the "H state of CO. (See note in proof for correction of the "ε+CO" curve.)

Fig. 7. Model atmosphere for CO₂, O and CO (the latter described by upper and lower limits). The dotted curve represents a hypothetical deviation of atomic oxygen from a diffusive equilibrium state in the lower thermosphere of Mars.
plotted in Fig. 6, from which the CO density at the reference level may be determined. We decided to use the "cold-emission" case as a means of establishing an "absolute" lower limit to the CO density. These values are $n$(CO, 150 km) > $3.2 \times 10^8$ cm$^{-3}$ and $n$(CO, 170 km) > $4.1 \times 10^8$ cm$^{-3}$.

4. Discussion

Stewart (1971) has presented a number of thermospheric temperature profiles for Mars, based on various possibilities for the partitioning of the absorbed solar ultraviolet energy. We have selected his intermediate model (A,O$_2^+$), in which the dissociation products are carried downward into regions of high density before they release their chemical energy of recombination. (The O$_2^+$ designation refers to the dominant ion composition in the model, which does not concern us here.)

The normalization of the CO$_2$ density is chosen in order for the CO$_2$ column density above 135 km to be $4.2 \times 10^{14}$ molecules cm$^{-2}$, a value consistent with the assumption of an F1 ionospheric peak occurring at 135 km (Barth et al., 1971) in accord with the results of the radio occultation experiment (Fjeldbo et al., 1970).

The concentrations of CO$_2$, CO and O are plotted in Fig. 7 using the assumption of diffusive equilibrium. The atomic oxygen curve corresponds to the 3% model. The dotted curve for O shows a hypothetical deviation from diffusive equilibrium, which might occur as a result of rapid eddy mixing in the lower thermosphere. This model was chosen to test the sensitivity of the radiative transfer calculations to changes in the density distribution in the 100–200 km region. Only a small change in the shape of the 1304 Å intensity curve was evident, demonstrating that radiative trapping effects tend to wash out details of the density profile. It also shows that the actual density of O at 135 km could be significantly smaller than 0.03 CO$_2$. The intensity measurements are much more sensitive to the O concentrations at high altitudes.

The upper and lower limits of the CO distribution are also shown in Fig. 7. These curves were obtained by passing a diffusive equilibrium curve through the previously derived values for the upper and lower limits on CO density at 170 km. At the ionospheric peak, the CO concentration is $\sim 0.3\%$ of CO$_2$, only one-tenth that of the O concentration. Because of its smaller scale height CO increases more rapidly than O with decreasing height. At about 100 km the CO:O ratio is unity. In order for the CO:CO$_2$ ratio to equal the value of $8 \times 10^{-4}$ derived from ground-based spectroscopic measurements (Kaplan et al., 1969), it is necessary to extrapolate the curve well below an altitude of 70 km. If the CO were well mixed in the atmosphere up to some "turbopause" altitude, this procedure suggests a low turbopause altitude, and, consequently, a low eddy mixing rate. However, as discussed by McElroy and Hunten (1970) and Hunten (1971), the low densities of O in the upper atmosphere of Mars can be explained in a satisfactory way only by invoking rather large eddy mixing rates. This possibility was first discussed by Shimizu (1968).

If the turbopause is much higher than 70 km, the assumption of a constant mixing ratio of CO in the lower atmosphere is not justified. It is reasonable to suppose that the CO concentration in the upper atmosphere is at least partially controlled by local processes of production and loss, and that their altitude variation would cause the CO mixing ratio to decrease with decreasing height.

No information on the lower atmospheric content of O is available [although Belton and Hunten (1968) place an upper limit of $2.6 \times 10^{-3}$ to the mixing ratio of O$_2$]. If the atmosphere of Mars is in a steady state, then the average column rates of both production and of loss of O and CO are equal. Ignoring the presence of O$_2$, this implies that the vertical column densities of O and CO are equal above any altitude in the eddy mixing regions, and, specifically, immediately above the turbopause. The altitude of the turbopause determined in this manner is 80–100 km, depending upon whether the intermediate value or upper limit is selected for the CO concentration. It should be pointed out that the upper limit on CO depends upon the adopted value for the resonance g factor of Table 1, which, in turn, relies upon the knowledge of the solar flux in the region between 1475 and 1525 Å. There is currently some question as to whether the values of solar flux in this spectral region quoted by Hinteregger et al. (1965) are too large by a factor of about 3. If this is indeed the case, the upper limit on the CO values would be trebled, and the altitude at which the column densities of O and CO are equal increases to about 120 km. The corresponding turbopause altitude is consistent with an eddy diffusion coefficient of $\sim 10^7$ cm$^2$ sec$^{-1}$, a value which may be sufficiently large to explain the low O concentration.

5. Summary

We have presented evidence from the UV spectrometer experiment that atomic oxygen and carbon monoxide are present in comparable amounts in the upper atmosphere of Mars. Our analysis shows that their concentrations in the thermosphere of Mars are only a few percent of CO$_2$, apparently a consequence of a high rate of downward transport from eddy diffusion processes. The CO mixing ratio probably decreases with decreasing height, from a value which may be as high as 1% at the F1 peak to less than 0.1% in the lower atmosphere. The O mixing ratio probably decreases with height in the same manner. The altitude where the column densities of O and CO are equal defines the approximate location of the turbopause, if the concentrations of secondary products of CO$_2$ dissociation (such as O$_2$) are small. Our analysis would therefore place the turbopause between the altitudes of 80 and 120 km.
Note added in proof: L. Wallace has pointed out that the transmission function $T(v',0)$, as defined here, neglects the effects of the splitting of the rotational lines into $P$- and $R$-branches. It can be shown that when one includes these effects, the net result is to replace the quantity $T(r_x)$ in Eq. (7) with an average transmission function, given by $0.5\left[T(0.25r_x) + T(0.5r_x)\right]$. This correction causes the transmission curve (labeled “$e$+CO” in Fig. 6) to be raised somewhat. The consequence for the “absolute” lower limit on CO density is to multiply the values given in the text by the factor 2.3.

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